

THE OXYGEN DEFECT PEROVSKITE $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$, A METALLIC CONDUCTOR

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ABSTRACT

A new oxygen defect perovskite $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$, characterized by a mixed valence of copper has been isolated; the parameters of the tetragonal cell are closely related to that of the cubic perovskite: $a = 8.644(4) \text{ \AA}$, $c = a_p \sqrt{5}$ and $c = 3.867(3) \text{ \AA} = a_p$. The X-ray diffraction study shows that the atoms are displaced from their ideal positions in the cubic cell, owing to the presence of ordered oxygen vacancies. The study of conductivity, magnetic susceptibility and thermoelectric power versus temperature shows that this oxide is a very good metallic conductor.

INTRODUCTION

Oxygen defect perovskites, have been more extensively studied these last years owing to their potential applications in catalysis, electrocatalysis or as gauges (1-3). In this respect mixed valence copper oxides offer a wide field for investigation: several perovskites (4) or perovskite-related structures have been isolated (5-6). These materials in which copper takes several coordinations simultaneously and a valence state intermediate between II and III can intercalate large amounts of oxygen according to the oxygen pressure and the temperature. Their electron transport properties ranging from semi-conductive to metallic (7) are closely correlated to the amount of intercalated oxygen.

The present paper deals with a new oxygen defect perovskite $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$, which is like $\text{La}_2\text{Ba}_3\text{Cu}_6\text{O}_{14.8}$ (4) a mixed valence copper oxide but whose behavior is quite different.

EXPERIMENTAL

Synthesis

Samples were prepared in platinum crucible and in air from appropriate mixtures of dried oxides La_2O_3 , CuO and carbonate BaCO_3 . The mixtures were first heated a few hours at 900°C , ground and heated at 1000°C during several hours. They were then ground again, and mixed with an organic binder, compressed into bars and then slowly heated up to 1000°C . After 24 hours or more at 1000°C , the bars were finally quenched to room temperature. The use of a binder was necessary to avoid that the compressed bars break before

heating. In these conditions the compactness of bars was of about 80 %.

Chemical analysis

In order to determine the oxidation state of the transition metal ions, chemical analysis were carried out by iodometric titration using KI and by reduction in a flow of 25 % hydrogen in argon up to about 1000°C using a SETARAM microbalance for weight loss measurements.

Structural analysis

The cell parameters were determined from X-ray powder diffractograms registered with a Philips goniometer using Cu K α radiation. The space group was determined by electron diffraction using a JEOL 120CX electron microscope.

Magnetic and electrical measurements

The magnetic susceptibility was measured on powders by the Faraday method in the range 80-300K using a Cahn RG microbalance.

The conductivity was measured by the four points method on sintered bars. It was calculated by measuring the intensity/voltage ratio between the points in each current circulation direction in order to minimise the dissymmetry effect between the contacts. The Seebeck coefficient was measured on the same sintered bars held between two Pt beads.

Measurements were carried out up to 600K under an helium pressure of 200 mbars for $T < 290K$ and in air for $T > 290K$ in order to avoid possible departure of oxygen.

RESULTS AND DISCUSSION

The scanning of the system $\text{La}_2\text{O}_3\text{-BaO-CuO}$ for the compositions corresponding to the molar ratio $(\text{La} + \text{Ba})/\text{Cu} = 1$ allowed us to isolate a perovskite for $\text{La/Ba} = 4$. The X-ray diffraction pattern of this compounds presents besides the intense lines which can be indexed in a cubic perovskite cell, extra lines which are rather weak. This feature is confirmed by the electron diffraction study, which shows superstructure reflections, leading to a tetragonal cell whose parameters are related to the cubic perovskite subcell (a_p) as follows :

$$a = a_p \sqrt{5} \quad c = a_p$$

all the lines of the X-ray diffraction patterns can be then indexed with accuracy in the tetragonal system with $a = 8.644(4) \text{ \AA}$ and $c = 3.867(3) \text{ \AA}$. No reflection conditions are observed. The analysis of the oxygen content leads to the formulation $\text{BaLa}_4\text{Cu}_5\text{O}_{13.4}$ involving the presence simultaneously of Cu(II) and Cu(III) in spite of the presence of numerous oxygen vacancies (10.7 %). The measure of the density by pycnometry in benzene at 25°C ($d_{\text{exp}} = 7.05$) confirms this composition for one mole per cell ($d_{\text{calc}} = 7.03$). Thus it appears that the oxide $\text{BaLa}_4\text{Cu}_{12.2}\text{Cu}_{11.6}^{III}\text{O}_{13.4}$ exhibits a great similarity with the oxygen defect perovskite $\text{Ba}_3\text{La}_3\text{Cu}_{15.26}\text{Cu}_{11.6}^{III}\text{O}_{14.6}$ previously described. However, this compound is very different from $\text{Ba}_3\text{La}_3\text{Cu}_6\text{O}_{14.6}$ from the point of view of the oxygen intercalation : no intercalation or desintercalation of oxygen has been observed by annealing this phase at low temperature (400°C to 500°C) and under different oxygen pressures up to 1 bar contrary to $\text{Ba}_3\text{La}_3\text{Cu}_6\text{O}_{14.6}$. In the same way, no oxygen loss has been observed by TGA measurements for temperatures up to 650, 750 and 850°C and under oxygen pressures of 0.02, 0.2 and 1 bar respectively.

Taking into account the fact that the fundamental lines are indexed in a cubic perovskite cell and are strong with respect to the superstructure lines it was interesting to determine whether the metallic atoms were displaced from their ideal positions in the perovskite, or if the superstructure lines

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were only due to the ordering of oxygen vacancies. However, owing to the small amount of oxygen vacancies it was not likely to determine the distribution of the oxygen atoms by X-ray powder diffraction. Thus the structural study was undertaken for the composition La₄BaCu₅O₁₅ just to determine the positions of the atoms with respect to the cubic perovskite subcell. Eight space groups were possible, they were reduced to three P4, P4 and P4/m taking into account the analogy with the perovskite structure. Calculations were carried out in the most symmetrical space group P4/m. For a ranging from 0 to 48°, 37 peaks i.e. 84 hkl were registered. The disparity between Fhkl and F hkl led us to introduce 139 hkl in the calculations. In the same angle range 13 diffraction peaks (14 hkl) were indexed in the cubic perovskite cell with a = 3.867 Å, and used in a calculation with the atoms in the ideal positions of the cubic perovskite cell, involving only a refinement of the thermal factors B; this first refinement led to a discrepancy factor $R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs.}}$ of 0.066 with B(La, Ba) = 1.2 Å², B(Cu) = 2.6 Å², B(O) = 3.9 Å². The high B values let us think that the atoms were displaced from their ideal positions. A calculation carried out with all the intensities in the P4/m space group and the same ideal positions and overall B = 1 Å² (Table 1a), led to R = 0.35 in agreement with this point of view. Starting from these ideal positions, and assuming a statistical distribution of the oxygen vacancies in the oxides BaLa₄Cu₅O_{13.4}, the R factor was lowered to 0.083, by refinement of the atomic parameters, the B factor being fixed at 1 Å². From the final atomic parameters (Table 1.b) it can be seen that several atoms are displaced from their ideal positions in the cubic perovskite.

TABLE 1

Atomic Parameters of BaLa₄Cu₅O_{13.4} (a) ideal positions (b) after refinement in the space group P4/m

Atom	Site	X	(a) Y	Z	X	(b) Y	Z
Ba, La	1(d)	0.5	0.5	0.5	0.5	0.5	0.5
Ba, La	4(k)	0.1	0.3	0.5	0.124(1)	0.277(1)	0.5
Cu	1(a)	0.0	0.0	0.0	0.0	0.0	0.0
Cu	4(j)	0.4	0.2	0.0	0.415(3)	0.168(2)	0.0
O	1(b)	0.0	0.0	0.5	0.0	0.0	0.5
O	2(e)	0.0	0.5	0.0	0.0	0.5	0.0
O	4(j)	0.3	0.4	0.0	0.261(7)	0.384(8)	0.0
O	4(j)	0.2	0.1	0.0	0.229(8)	0.063(6)	0.0
O	4(k)	0.4	0.2	0.5	0.428(10)	0.155(6)	0.5

Further refinements, concerning the ordered distribution of oxygen in this structure, which is most probable, were not carried out due to the rather low content of oxygen vacancies, and the too small number of reflections.

This oxide is a very good conductor: its conductivity is about $1.6 \cdot 10^3 (\Omega \text{ cm})^{-1}$ at room temperature. Figure 1 which represents the resistivity ρ versus temperature, shows that this oxide exhibits a metallic conductivity from 200 to 600K. The γ value deduced from the equation $\rho = \rho_0(1 + \gamma t)$ ($\gamma = 4.1 \cdot 10^{-3} \text{ C}^{-1}$) is very close to that of free electrons ($\gamma = 3.7 \cdot 10^{-3} \text{ C}^{-1}$).

The molar magnetic susceptibility is very weak and nearly independent of temperature. This suggests a Pauli paramagnetism which is characteris-

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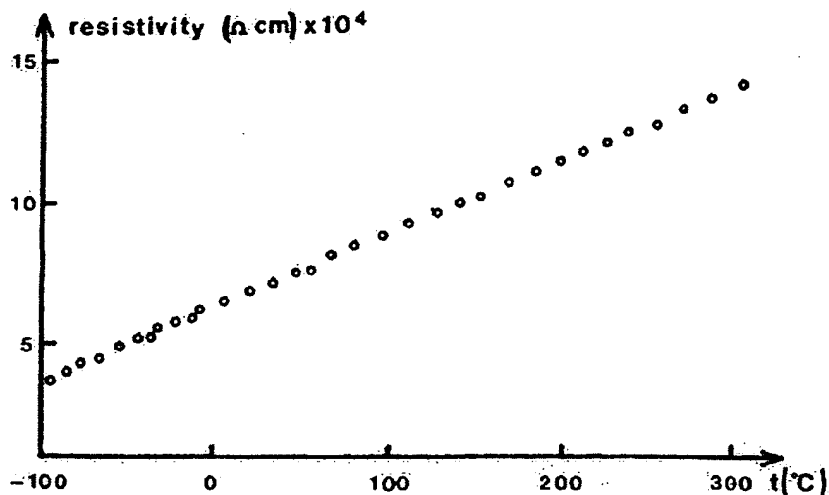


FIG. 1

Resistivity plotted as a function of temperature

tic of delocalized carriers. The Pauli susceptibility (8) calculated with $m^*/m = 1$ and for one carrier per Cu(III) ($\chi_M = 5.3 \cdot 10^{-5}$ e.m.u) is however one order of magnitude lower than the experimental value : $\chi_M = 6 \cdot 10^{-4}$ e.m.u. The increasing of the Pauli susceptibility up to the experimental value needs $m^*/m = 10$. This suggests a strongly correlated carriers gas (degenerated spin polaron gaz) which was introduced by Mott (9) to explain the magnetic susceptibility of LaCuO_3 and LaNiO_3 which are metals (10). At room temperature, the Seebeck coefficient is also very weak and positive ($\alpha = 9 \mu\text{VK}^{-1}$) and increases slightly with temperature ($\alpha_{500\text{K}} = 18 \mu\text{VK}^{-1}$) (Fig. 2). This

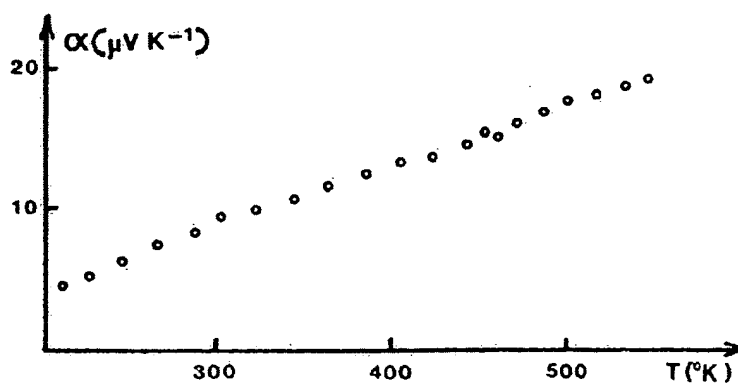


FIG. 2

Evolution of the thermoelectric power as un function of absolute temperature.

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